

Report for 2004WA75B: Phosphorus Contamination of Surface Waters

- Water Resources Research Institute Reports:
 - Flury, Markus, Claudio O. Stockle, Joseph Harriason, and James Harsh. 2005. Phosphorus Contamination of Surface Waters, State of Washington Water Research Center, Washington State University, Pullman, Washington, Water Research Center Report No. WRR-24, 30 pp.
- Dissertations:
 - Jerez Briones, Jorge, 2005. Aluminosilicate-Coated Silica Sand for Reactive Transport Experiments, PhD Dissertation, Washington State University, Pullman, WA, 135 p.
 - Mejias, Jaime H., 2005. Phosphorus Leaching from Manure-Impacted Soils Affected by Fluctuating Water Tables, PhD Dissertation, Washington State University, Pullman, WA, 155 p.

Report Follows

PROBLEM AND RESEARCH OBJECTIVES

Long-term application of dairy manure to farmland has caused an accumulation of P in soils. There is a potential risk of P release to the soil solution and subsequent leaching of P out of the soil into surface waters, especially where seasonal flooding occurs. While many P sorption studies have been conducted, the influence of redox reactions on P chemistry and its potential impact on P movement into tile drains has not been investigated intensively. We hypothesized that soils containing high P levels release a considerable amount of P during flooding, thereby posing a latent risk for surface water eutrophication.

The goal of the proposed research was to study fate and transport of P in soils characterized by periodic anaerobic conditions. Specifically, we addressed the following objectives:

- Acquire relevant field data to understand the dynamics of dissolved P in tile effluents.
- Explore the effect of the soil redox potential on P release and transport in soils.
- Develop a tile-drain filter to reduce the concentration of dissolved P in tile effluents to comply with EPA water quality criteria.

METHODOLOGY

Field Study

Two dairy farms, typical for dairies in the Pacific Northwest, were selected as the experimental sites. We denote the field sites as Everson and Lynden. The soil series were identified as Pangborn muck and Briscot series, respectively. Dry soil bulk density was measured in the top soil (0-10 cm) using the intact core method, and soil texture was determined using a soil particle size analyzer. Soil samples for chemical analyses were taken at two depths (0-30 cm and 30-60 cm) with a manual auger. Soil pH was measured in a 1:2 (w/v) soil:water solution. Total organic carbon (TOC) and total organic nitrogen (TON) were determined in a Leco FP2000 Nitrogen and Carbon Analyser. Plant available P was measured with the Bray and Kurtz P-1 (Bray-P1) method according to standard procedures. Calcium-chloride-extractable P, oxalate extractable P, iron and aluminum were also obtained. Soil P sorption characteristics were assessed by performing P sorption isotherms and calculating the degree of saturation of the P sorption capacity of the soils. We installed nine tensiometers at soil depths of 25, 50, and 100 cm with three replicates each. The tensiometers were located five meters away from the ditch. The water tension inside the tensiometer was measured every 15 days with a pressure transducer and a digital display. At each location, two tile drains were selected and the outflow of the drains into the drainage ditch was monitored. At the Everson site the two drains were located in a pasture and a corn field each. The corn field was located right next to the pasture. Samples were collected from April 2004 through February 2005, with a sample frequency of 15 days. The flow rates were measured manually using a bucket and a stop watch with three replicates per tile drain. Weather data during sampling were collected in an automatic weather station.

Column Study

The effect of redox potential on P fate and transport was investigated using a laboratory column flow-through system. We used ferrihydrite-coated sand as porous medium and controlled redox

potential using Fe-reducing bacteria. Phosphorus was sorbed onto the ferrihydrite with an initial breakthrough experiment, and the P release, caused by changes in redox potential and subsequent transport, was monitored in the column outflow. We determined P sorption isotherms on the ferrihydrite-coated sand in batch systems with 15 mM KCl background solution and two replicates at two different pH values: 4 and 7. Small columns of 1-cm i.d. and 10-cm length were packed with the ferrihydrite-coated sand. The column system was kept O₂-free by using air-tight N₂ boxes. We maintained a constant upward-flow by a peristaltic pump at a flow rate of 0.035 cm/min (=0.5 m/d). Redox potential and pH were monitored in five minute intervals with in-line electrodes connected to flow-through cells. The system was setup in a temperature-controlled growth chamber at 10°C under dark conditions to mimic soil conditions.

Column outflow was analyzed for Fe²⁺, P, and turbidity (bacteria concentration). We performed XRD analysis to determine secondary mineral formation. At the end of the experiments, the column was dissected in 4 increments and the 6 M HCl soluble Fe and P were measured colorimetrically. Phosphorus batch sorption isotherms were analyzed with the Langmuir isotherm.

The solubility equilibrium of the precipitates originated from the biogenic iron reduction and the stable solid mineral phases were predicted with the chemical speciation program Visual MINTEQ. Different cases were considered for modeling: (1) three combinations of low, medium and high concentrations of P, and (2) chemical speciation of solid phases in three different stages of the elution P curve.

Experimental breakthrough data of P transport were analyzed using the software package Hydrus-1d. Hydrus-1d numerically solves the Convection Dispersion Equation (CDE) for solute transport assuming linear and nonlinear non-equilibrium solute sorption. We selected the two-site sorption option. Hydrus 1-d was run both in direct and inverse mode using the sorption data obtained from batch experiments.

Filter design experiment

We tested a filter that can remove P efficiently from water flowing through a tile drain. Ferrihydrite has a large sorption capacity for P and is a useful filter material. The postulated filter uses ferrihydrite-coated sand. The ferrihydrite provides the sorption sites for P removal, while the sand matrix allows adequate water flow. We envisage that the filter consists of two PVC tubes that are installed at the tile-drain outlet. The first tube acts as a sediment trap (physical removal of sediments due to sedimentation). The second tube would contain ferrihydrite-coated silica sand.

We used the ferrihydrite-coated silica to test its P sorption capacity when used in a filter. In a column experiment the total capacity of the filter was obtained by integration of the elution P curve. Calculations were based on measured water flow rates in tile drains and measured saturated hydraulic conductivities of ferrihydrite-coated silica sand. The life-time of the filter medium was estimated using annual P (dissolved orthophosphate) loading data from the Lower Nooksack drainage area. We considered 5 tile lines per ha, and one filter per tile drain line. We also developed a methodology to coat hematite onto silica sand. Then we tested a hematite-coated sand filter media to increase the P sorption capacity.

PRINCIPAL FINDINGS AND SIGNIFICANCE

The principal findings of this study are listed in itemized form below.

Field Study

- Mean P concentrations in drainage waters revealed that molybdate reactive P concentration in tile drain outflows was greater than eutrophication limits and likely associated with Fe^{2+} concentrations. P was released due to reductive dissolution of iron-P complexes, which was supported by the decrease in redox potential of the drainage water (Figure 1) and the periodic flooding detected by the soil water tension data (Figure 2).
- Monitoring data from the pasture system confirmed our hypothesis that in soils enriched with P and affected by fluctuating water tables, P is released as a result of iron reduction and transported off site via tile drains as indicated by the positive correlation between P and Fe^{2+} (Figure 3). In the corn field, Fe^{2+} was detected in the drain outflows but it was not related to P. Instead, a good correlation was found between P and Fe^{3+} , indicating that different processes affect the P release in cultivated soils.
- According to the light scattering analysis no colloids were detected in the water samples. It appears that P was transported in dissolved forms or in complexation with dissolved organic matter. We suspect that the release of P and Fe^{3+} to solution was a result of abiotic dissolution of iron phosphate minerals by dissolved organic matter rather than reductive dissolution. After dissolution P could have been transported in complexation with iron and dissolved organic matter.

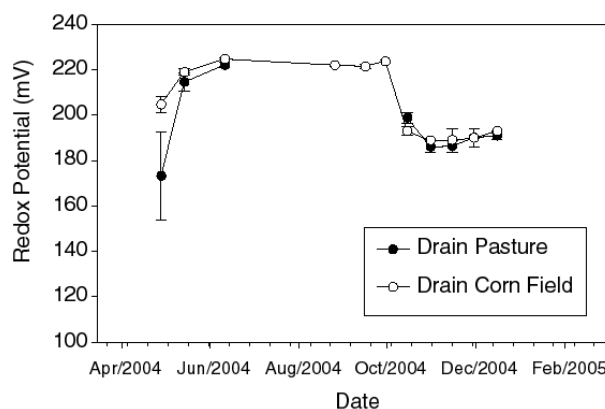


Figure 1: Redox potential in tile drain outflow.

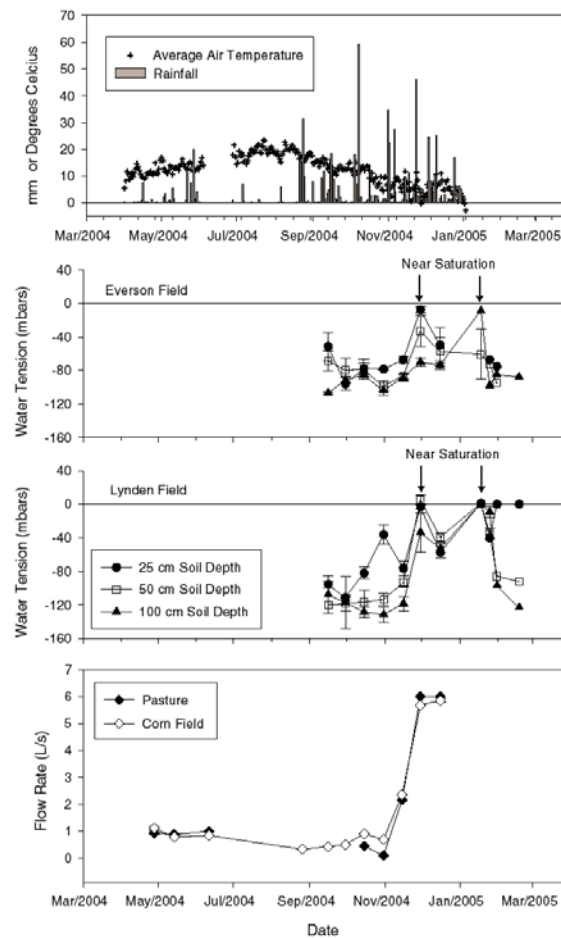


Figure 2: Temperature, rainfall (top), water tension (middle) in Everson and Lynden sites, and flow rate measured in the drain outlet in Everson site (bottom).

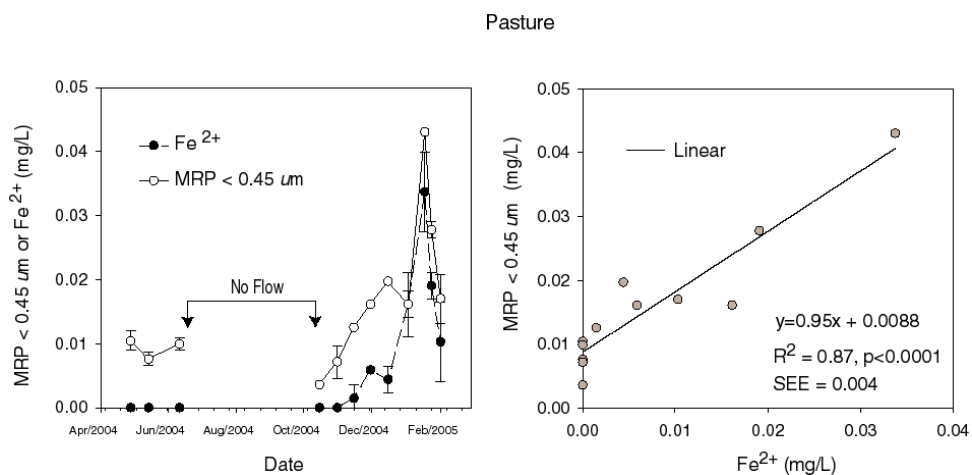


Figure 3: Molybdate-reactive P (MRP) and Fe^{2+} relationship in tile drain outflow from the pasture system in Everson.

Column Study

- We found that upon biotic reductive processes of P-bearing (hydr)oxides, P is released and mobilized during dynamic flow conditions. The redox potential of the P-saturated system was reduced by introducing Fe-reducing bacteria. The redox potential started to drop after 105 pore volumes, the net P leached out during the reductive part of the experiment was 0.19 μ moles (Figure 4). In relative terms, the amount of P lost during the reductive part of the experiment represents the 7 % of the total P in the column prior to the introduction of bacteria.
- An initially anaerobic system retained more P than the oxidized column due to precipitation reactions. However, the dissolution of the precipitated phases during the re-oxidation of the column caused release of most of the P fixed during the reductive period. Overall, a reduced environment fixed less P than an oxidized environment.
- Systems initially oxidized, under dynamic flow conditions and containing high amounts of chemisorbed P, represent an environmental risk when redox potentials are dropped below the point of Fe reduction (180 mV).
- Phosphorus initially fixed in a reductive environment is released more readily when oxic conditions are recovered, compared to P initially fixed in an oxidized environment.

Filter design experiment

- Preliminary experiments indicate that ferrihydrite-coated silica can remove 0.04 mg P/(g of sand) at 10°C for sand particles of diameters between 0.25 and 0.5 mm. Calculations based on measured water flow rates in tile drains and measured saturated hydraulic conductivities of a ferrihydrite-coated silica sand (grain diameter between 0.25 and 0.5 mm, $K_s = 40$ cm/h), show that the filter can remove in total 4 g of P. A schematic of the proposed filter is shown in Figure 5.
- Considering an average of 5 tile lines per ha, and an annual P (dissolved orthophosphate) loading from the Lower Nooksack drainage area of 215 g/ha, we conclude that the sorption capacity of the filter is not enough to remove the bulk of the orthophosphate from the drain discharge.
- We therefore increased the sorption capacity of the filter by developing a methodology to coat silica sand with hematite instead of ferrihydrite. Hematite is smaller and has a greater surface area than ferrihydrite and can therefore remove more P. The P sorption capacity increased by a factor of 10, so that the filter can now remove 40 g of P, which allows us to remove the bulk of the orthophosphate from the drain discharge. The different filter capacity for P of hematite and ferrihydrite is illustrated in Figure 6.
- We estimate that the filter has to be replaced once year. Dissolving the iron by reductive processes may recycle the P retained in the filter.

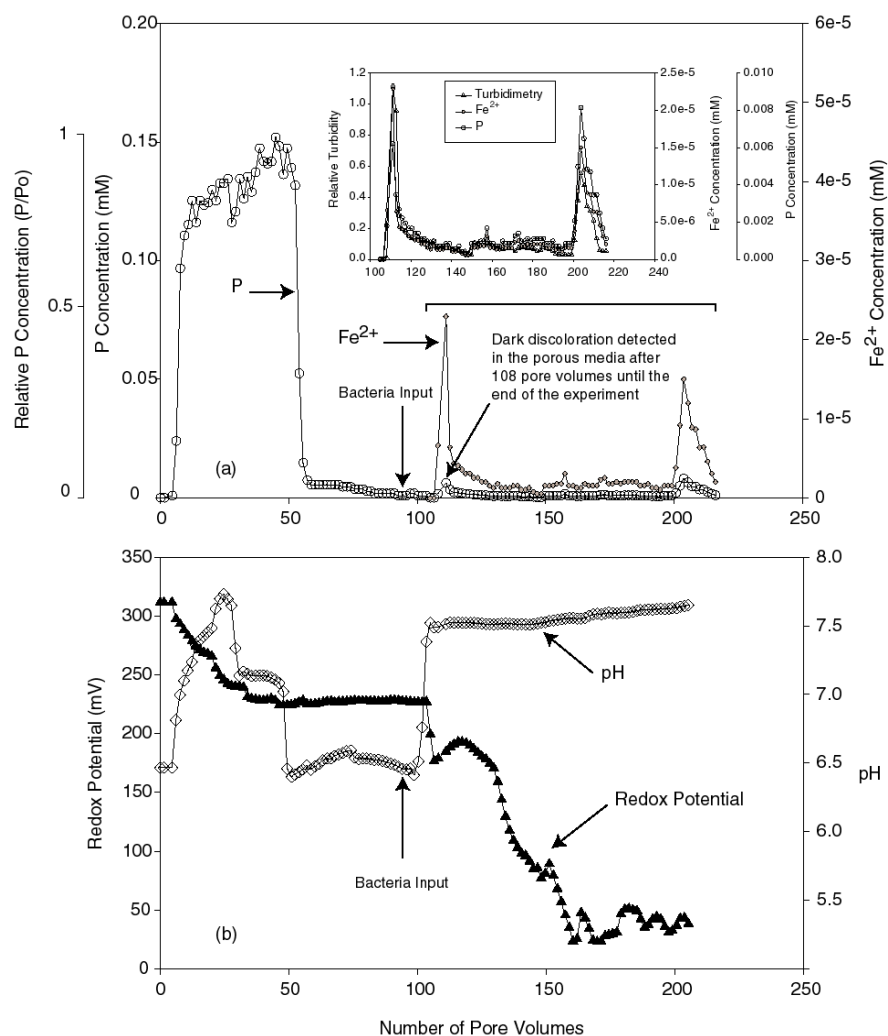


Figure 4: Phosphorus release from a P-saturated ferrihydrite coated sand column after biogenic iron reduction (top). Redox potential and pH variation during the experiment (bottom).

Significance of study

Release of P from agricultural lands to water ecosystems impairs surface water quality. The reductive dissolution of ferric iron associated with P is postulated as a mechanism controlling P transport and fate in manure-impacted soils affected by flooding. In this study we provide evidence that P was released upon ferric iron reduction in a pasture system as indicated by the significant relationship between P and ferrous iron. This evidence was corroborated in lab experiments where P was released upon iron reduction under dynamic flow conditions. These results confirm that redox processes are important mechanisms controlling the P transport and fate in agricultural soils. We found that the P levels in the drain outflow were higher than the 0.01 mg/L defined as a critical environmental limit. Therefore, this study suggests that soils with elevated P iron-bearing materials affected by anaerobic conditions should receive special management to avoid the redox potential decrease below critical limits. This study also proposes a remediation for controlling critical limits of P in the drainage water.

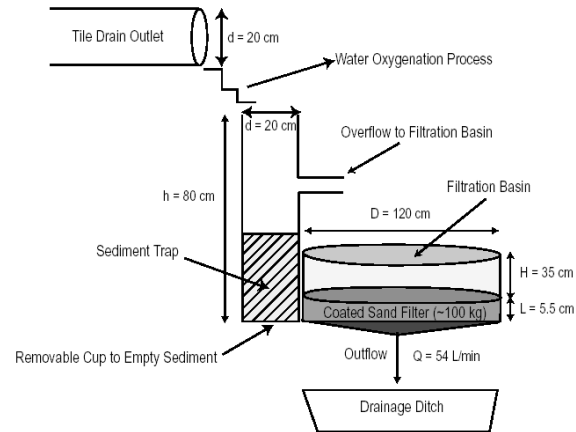


Figure 5: Schematic of the filter design to remove P from tile-drain outflow.

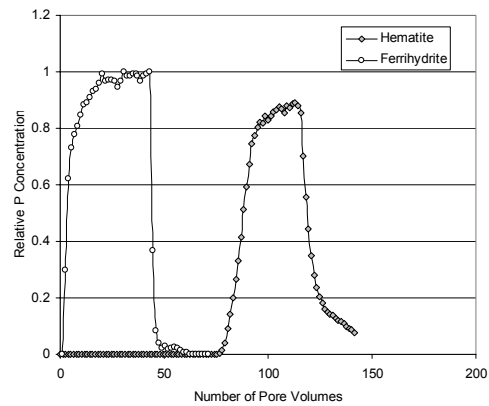


Figure 6: Phosphorus retention in porous filters made of hematite- and ferrihydrite-coated sands.